AD-A178 864 ASSEMBLY AND FUNCTIONALIZATION OF SUPRAMOLECULAR STRUCTURES STUDIED BY LUMINESCENCE TECHNIQUES(U) EUROPEAN RESEARCH OFFICE LONDON (ENGLAND) F C DE SCHRYVER 15 JAN 87 DAJA45-84-C-0012 F/G 7/3 1/1

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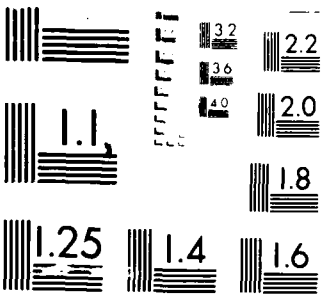

ASSEMBLY AND FUNCTIONALIZATION OF SUPRAMOLECULAR STRUCTURES STUDIED BY LUMINESCENCE TECHNIQUES

Final Report

by

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I. Introduction

II. Aggregation mechanism, CMC and role of additives

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I. INTRODUCTION

Species of colloidal dimensions like micelles, inverted micelles or microemulsions are formed in aqueous or non-aqueous media when a certain concentration of monomers also called tensides, amphiphiles or detergents, has been exceeded. This concentration is called the CMC or critical micellar concentration.

This aggregation of monomers is a result of the typical structure of a detergent molecule, that combines a hydrophilic part (the polar headgroup) with a hydrophobic part (the apolar tail). The size and shape of the aggregates formed is strongly dependent upon the molecular structure of the monomers that are building up such a micelle and evenso upon the medium used and upon the presence or absence of additives.

The ability of forming aggregates makes these detergent molecules responsible for typical practical applications like e.g. detergency, foaming, increasing (catalysis) or decreasing (inhibition) the speed of an organic reaction. Also these aggregates can be used for mimicing systems of biological structures like mono- and bilayers, membranes, proteins, enzymes,...

One of the most important features, which is also the subject of study in this project; is the stability of the aggregates formed, and more especially the factors that account for the differences in structure and stability of the known inverse micellar system. Within the framework of this project new detergents were synthesized and probe/quencher systems, used for fluorescence studies, are evaluated to see in how far they can provide a better understanding of the aggregation behaviour and of the structure aspects that determine aggregate stabilization.

II. AGGREGATION MECHANISM OF INVERTED MICELLES

II.a. Theoretical aspects of the aggregation mechanism of ionic detergents in alkane / H_2O

For the aggregation of ionic amphiphiles in apolar media there have been proposed 3 models :

1) The mass-action (MA) model (Fendler 1982) which assumes the existence of an equilibrium between a micellar species A_n with an aggregation number n and the monomers A_1 obeing :

$$n\ A_1 \rightleftharpoons A_n \qquad \text{with an equilibrium constant : } K = [A_n] / [A_1]^n$$

2) The stepwise aggregation (SA) model (Hilhorst - 1982, Kalyanasundaran - 1984) describes the aggregation phenomenon as a successive addition of monomers to the aggregate:

$$A_1 + A_{n-1} \rightleftharpoons A_n \qquad (n = 2, 3, \ldots)$$

with an equilibrium constant

$$K_n' = [A_n] / ([A_{n-1}][A_1])$$

3) The model of Eicke (E-model) (Langevin 1984, Fendler 1984, Geladé 1984, Eicke 1979, Kon-no 1983, Verbeeck 1986).
In this model the aggregation starts from nuclei having three monomers that form, by a kind of SA mechanism, linear aggregates; these linear aggregates undergo, at higher surfactant concentration, a transformation to cyclic inverse micelles (figure 1).

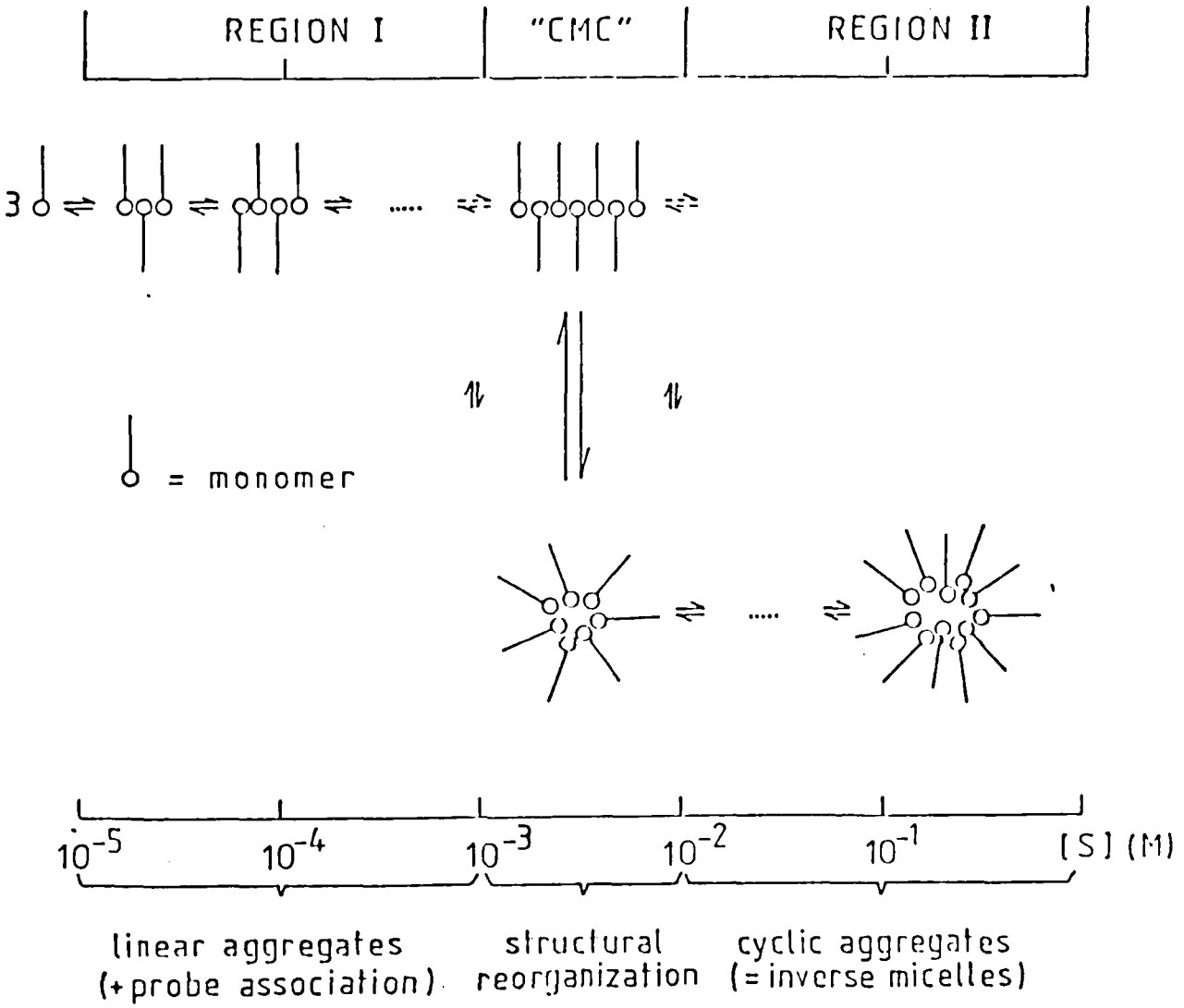


Fig.1 : The aggregation mechanism for AOT in cyclohexane as proposed by Eicke (Eicke 1979)

In this kind of model of course, the concept of the CMC, as the concentration where micelles are formed, has lost its original meaning. In this model however there has been introduced an "operational CMC" : this is the surfactant concentration where the transformation to cyclic units occurs.

II.b. Determination of the CMC using spectroscopic methods

To determine the CMC in reversed micellar systems one can use the variation of the absorbance of a (fluorescent)probe in function of the detergent concentration and the variation of the fluorescence lifetimes and preexponentials in function of detergent concentration. Plots of the absorbance and fluorescence lifetime versus the logarithm of the detergent concentrations (see figure 2) provide information on the CMC. Furthermure the influence of addition of H_2O (R-values) on the CMC can be investigated.

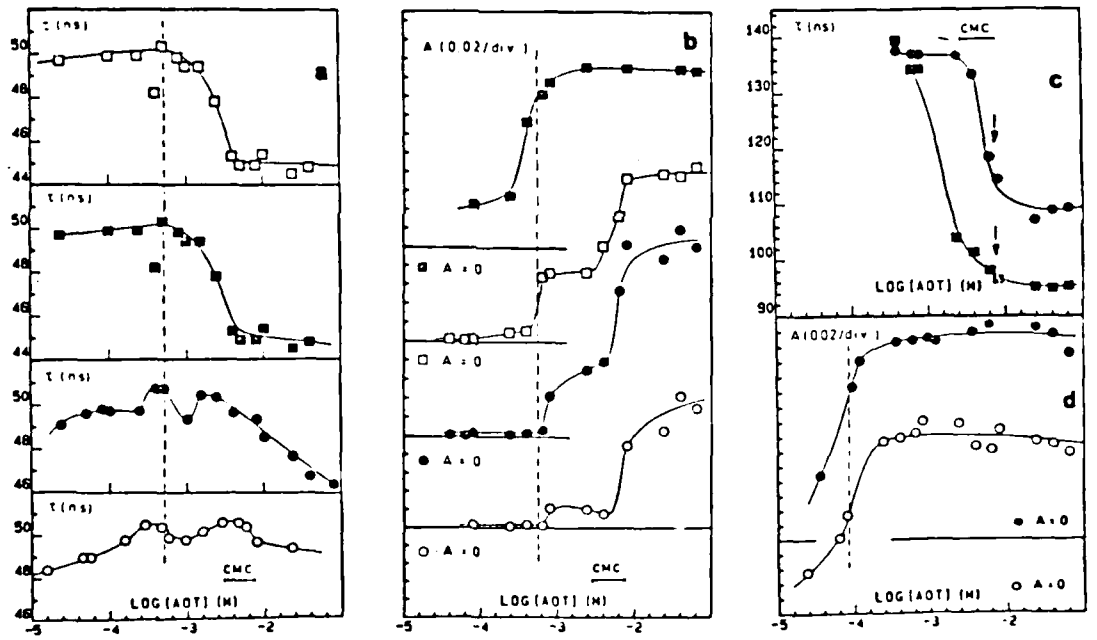


Figure 2 Influence of water on solutions of AOT in c-C_6H_{12} on (a) the fluorescence decay parameter (τ) of NAA, (b) the absorbance (A) of PSA^-Na^+, (c) the fluorescence decay parameter (τ) of PSA^-Na^+, and (d) the absorbance (A) of NMA^+Cl^-. Four concentrations of water were evaluated: $R = 0$ (○), $R = 3.7$ (●), $R = 6.8$ (■), and $R = 13.8$ (□).

In reversed micelles, derived from quaternary ammonium derivatives, the fluorescence decay of the probes used is no longer a one-exponential. The existence of a short and long lifetime can be explained in figure 3 by two possible associations of the probe and the ionic headgroups.

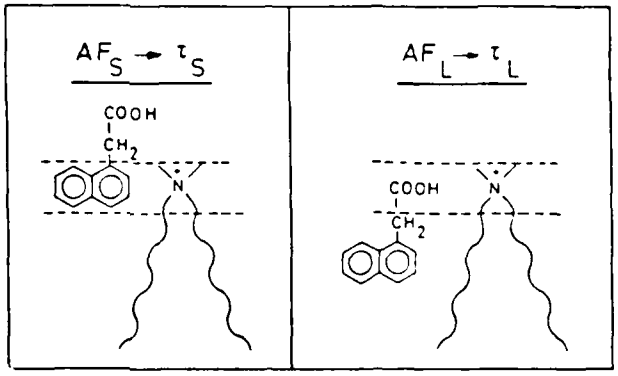


Figure 3 : Two possible association forms (AF) of NAA with the tetraalkylammonium head group of DDDAC, resulting in either a short (s) or a long (l) fluorescence decay parameter (τ).

The influence of addition of water upon the CMC of DDDAC (=DDAC) has been given in figure 4 and the determination of the CMC of DDDAC itself by lifetime measurements has been given in figure 5.

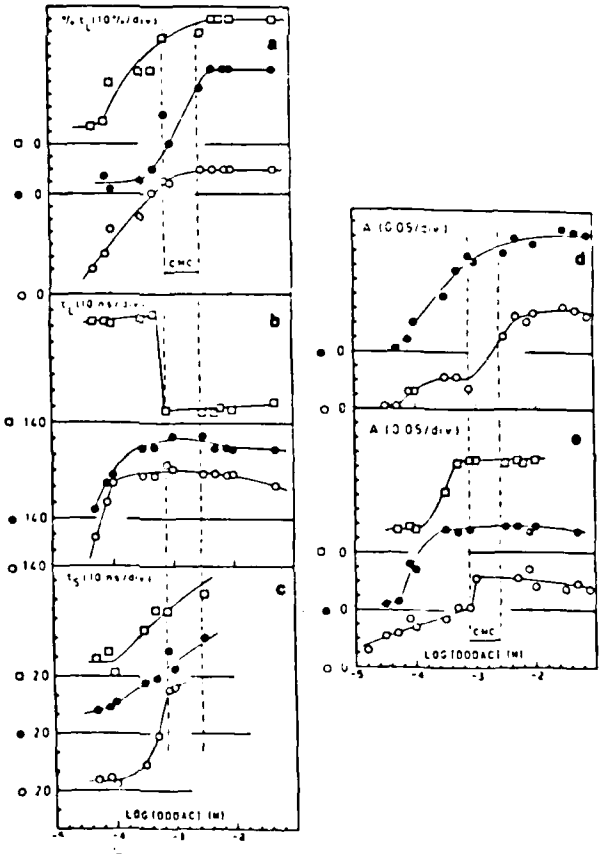


Figure 4 : Influence of water in solutions of DDDAC in c-C_6H_{12} on (a) the contribution (%) of the long fluorescence decay parameter (τ_l), (b) the long decay parameter (τ_l), (c) the short decay parameter (τ_s), (d) the absorbance (A) of PSA Na^+, and (e) the absorbance (A) of NMA^+Cl^-. Three concentrations of water are examined: R = 0 (○), R = 1 (●), and R = 40 (□).

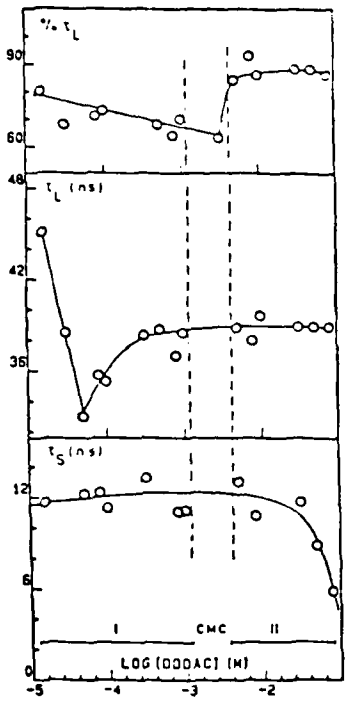
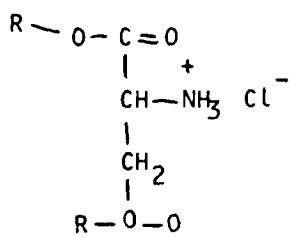
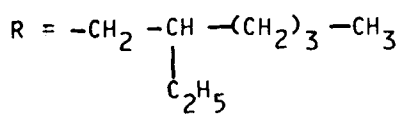


Figure 5 : Influence of the DDDAC concentration in c-C_6H_{12} on the contribution (%) of the long fluorescence decay parameter (τ_l), the long decay parameter (τ_l), and the short decay parameter (τ_s) of NAA.

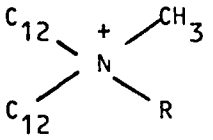
The CMC of the in the laboratory synthesized cationic analogue of AOT has also been determined by absorbance measurements and using decay times and the preexponentials obtained from the curve fitting and is found to be 8.10^4 M.





Cat. AOT

Using these techniques the CMC values of different ammonium derivatives of the following type were determined (table I)



	R	CMC
DDEAc	$-CH_2-CH_2-OH$	2×10^{-4} M
DDAcr.Ac	$-CH_2-CH_2-O-C-C=CH_2$ (O)	3×10^{-4} M
DDzAc	$-CH_2COOH$	9×10^{-4} M
DDAC	$-CH_3\ Cl^-$	2×10^{-3} M
DDAB	$-CH_3\ Br^-$	3×10^{-3} M

Table I : CMC values for didodecyl, methyl, R ammonium X^- detergents

From the obtained data it can be concluded that the cationic detergents also aggregate according to Eicker's model.

III.c. Solubilization of additives other than water in the micellar core

Evaluation of AOT

In industrial applications it can often be useful to replace the water in the interior of the inverse micel by other molecules. To investigate the solubilisation capacity of AOT/alkane mixtures different solvents were added to transparant solutions of about 0.08 M AOT in n-hexane, c-hexane and isooctane. For each amount added the R-value, this is $\frac{[\text{additive}]}{[\text{AOT}]}$, was calculated.

For most of the additives at a certain concentration of additive, at R_{max}, the solution becomes cloudy, indicating a phase separation. These R_{max} values for different additives are reported in table II. It is noteworthy that, in general, there is a tendency of increasing R_{max} values with diminishing polarity. Water is an exception in every solvent, probably due to its very small molecular volume and its very high ability for hydrogen binding.

Table II : R_{max} values for AOT solutions with [AOT] = 0.03 M in three different solvents at 20°C and the dielectric constant values for the different additives.

Solvent / Additive	n-hexane	c-hexane	isooctane
H_2O	70	30	78.5
DMSO	1.5	2	1.3
Glycol	1.8	3.9	2
Acetonitrile	12	7.2	8
DMF	6	10.8	5
MeOH	23.5	20	12
EtOH	> 220	> 360	> 316
Acetone	> 170	> 218	> 250
Isopropanol	> 283	> 250	> 240
n-Butanol	> 500	> 190	> 202
THF	> 380	> 196	> 225

III. FLUORESCENCE QUENCHING IN INVERTED MICELLES

The quenching of the fluorescence of an, in the micellar medium solubilized chromophore, has already many times been proven to be a useful and sensitive tool in the investigation of dynamic processes in micellar solutions.

After a δ-pulse excitation the intensity of the fluorescence as a function of time can be described by equation 1 :

$$I(t) = A_1 \exp\left[-A_2 t - A_3 \left(1 - \exp(-A_4 t)\right)\right] \quad (1)$$

with

$$A_1 = I(t=0) \quad (2)$$

$$A_2 = k_o + \frac{k_e k_{qm}}{A_4} [Q] \quad (3)$$

and

$$\frac{k_e k_{qm}}{A_4} = S_2 \quad (4)$$

$$A_3 = \frac{k_{qm}^2}{A_4^2} \frac{N_{agg}}{(\text{Detergent})} \cdot [Q_t] \quad (5)$$

and

$$\frac{k_{qm}^2}{A_4^2} \frac{N_{agg}}{(\text{Detergent})} = S_3 \quad (6)$$

with

k_o = $1/\tau_o$ (τ_o = fluorescence lifetime in absence of quencher)
k_c = exchange rate of quenchers between micelles ($s^{-1}M^{-1}$)
k_{qm} = fluorescence quenching rate constant (s^{-1})

These relationships are based on the following possible processes that can occur in a micelle with n quenchers and one excited probe

Process	Rate
$P_n^* \rightarrow P_n$	$k_o[P_n^*]$
$P_n^* \rightarrow P_n$	$nk_{qm}[P_n^*]$
$P_n^* + M_j \rightarrow P_{n+1}^* + M_{j-1}$	$jk_e[P_n^*][M_j]$
$P_n^* + M_j \rightarrow P_{n-1}^* + M_{j+1}$	$nk_e[M_j][P_n^*]$

with

P_n^* : a micelle with n quenchers and one excited probe

M_j : a micelle with j quenchers and no probe

where the probe and quenchers are Poisson distributed over the micelles and the chance of having a micelle with n probes (or quenchers) is given by :

$$P(n) = \frac{[M_n]}{[M]} = \frac{\mu^n e^{-\mu}}{n!} \qquad (7)$$

with

$[M]$ = total micellar concentration

$[M_n]$ = concentration of micelles with n probes (quenchers)

This scheme assumes that the solubilized probes neither the quenchers interact specifically with each other nor perturb the properties of the micelle; this is experimentally accomplished by working at low concentrations of probe ($\approx 10^{-6} - 10^{-5}$M) and quenchers ($10^{-5}$-$10^{-3}$M). When we assume that $k_{qm} >> k_c[M]$ the parameters in relations [1-6] simplify to :

$$A_1 = I_o \tag{8}$$

$$A_2 = k_o + k_e[Q_t] \tag{9}$$

$$A_3 = [Q_t] / [M] \tag{10}$$

$$A_4 = k_{qm} \tag{11}$$

The experimental setting does not allow a real δ-pulse excitation so that the actual fluorescence intensity in function of time t has to be described by a convolution of the "time" decay with the experimental IRF (instrument response function) pattern :

$$F(t) = \int_{u=0}^{t} I(t)\ IRF\ (t-u)\ du \tag{12}$$

A non-linear iterative reconvolution least square analysis allows the calculation of the A-parameters from the experimentally measured F(t) decay curve.

Of course the fluorescence quenching method has got its own characteristic possibilities and limitations.

It should be emphasized that the choice of a probe/quencher combination is crucial for the successful use of this fluorescence quenching method. Too bulky probes and/or quenchers cause a disturbance of the (small) reverse micellar aggregates leading to incorrect values of N_{agg}. For this reason the system $Ru(bpy)_3^{2+}/Fe(CN)_6^{3-}$ has to be avoided for the characterization of inverse micellar aggregates.

If dynamic quenching occurs, the efficiency of a probe/quencher system is related to the quenching rate constant of the system in the micellar aggregates. For small aggregates (N_{agg} < 80) all probe/quencher combinations proposed are efficient. Because of the small micellar volume, the probability of collision of probe and quencher (k_{qm}) is sufficiently high for all systems proposed. At these small R-values, using PSA as probe, more information is available compared to PSTA as probe. The long fluorescence lifetime of PSA allows the measurement of the relative low k_e of these aggregates ($k_e < 10^9 M^{-1} S^{-1}$). This is not possible with the short living PTSA.

For the large aggregates (N_{agg} > 80), PTSA with a negative quencher is the only effective system for AOT in n-hexane. In AOT reverse micellar aggregates both PTSA and I^- or SCN^- are repelled from the interphase. The high k_{qm} for these probe/quencher systems results from the fast diffusion in the "free" water of the micellar waterpool. This is in contrast to a slower diffusion of positive quenchers which are attracted to the interphase of AOT. Therefore, an efficient probe/quencher system must be chosen in function of the surfactant system studied and more precisely in function of the charge of the polar headgroup.

The use of fluorescence quenching for the characterization of reverse micellar aggregates is limited by the dynamics of those aggregates. In the case of $k_e[M] > k_{qm}$, no correct information for N_{agg} and k_e can be obtained from the fluorescence decay of the probes in these micellar aggregates. For an even higher exchange rate, $k_e [M] >> k_{qm}$, the fluorescence decay of a probe is one-exponential. Only values for k_e can be obtained from these decay curves.

The results indicate that upon application of fluorescence quenching for the characterization of reverse micelles and w/o-microemulsions, the choice of the probe/quencher system is crucial. For the study of aggregates of AOT, from the four probe/quencher combinations proposed, PTSA in combination with a negative quencher (I^- or SCN^-) is the most effective system. This probe/quencher system allows the determination of N_{agg} and k_e of the aggregates with $R < 20$. The systems PTSA/Cu^{2+} and PSA/Cu^{2+} can only be used for the correct description of smaller aggregates ($R < 11$). Comparison of the four systems suggests boundary conditions that are important for the choice of an effective probe/quencher combination.

First it can be stated that a high value of k_{qm} is an absolute necessity for an effective probe quencher system. This is required because the concentration of quencher must be sufficiently low so that maximal one quencher per micel is solubilized. Since quenchers are distributed over the aggregates according a Poisson distribution, the average number of quenchers per micel, $[Q_t] / [M]$, can be maximal 0.3. Intermicellar exchange can then only result in the difference of one quencher per micel. Exchange of one quencher per micel during the lifetime of the probe is incorporated in the kinetic scheme of luminescence quenching here proposed, while exchange of two or more quenchers is not considered. This explains the deviations of linearity for A_2 and A_3 as a function of the quencher concentration if $[Q_t] / [M] > 0.3$.

Because of these low quencher concentrations required, parameter A_3 would be negligible and equation (1) (non-exponential decay) would reduce to equation (13) (one-exponential) unless k_{qm} is sufficiently high. From the results obtained in this work, the factors that determine the value of k_{qm} will now be discussed.

For all probe/quencher systems considered, k_{qm} decreases as the size of the aggregates increases. This variation is logical since each aggregate contains maximal one quencher and therefore the local concentration of quencher decreases as the size of the aggregates increases.

Not only the size, but also the heterogeneous interior of the reverse micellar aggregates determines the value of k_{qm}. In the aggregates that are built up with ionic surfactants, an electric double layer surrounds the waterpool. This electric double layer creates an electric gradient in the waterpool, radially varying from the interphase to the centre of the aggregate. This electric field increases with increasing size of the waterpool.

As a consequence, the location of ions in the waterpool is a function of their charge. In the case of AOT inverse micelles that have a negative charged interphase, positive ions are bound to the interphase while negative ones are repelled and therefore preferentially located in the centre of the micelle. The strength of these electric forces are determined by the charge of the ions and the strength of the electric field (i.e. the size of the aggregate). As a consequence, PTSA, I^- and SCN^- are located in the centre of the waterpool while Cu^{2+} is bound to the interphase.

Since the electric field hinders the diffusion of Cu^{2+} ions to the probe PTSA, k_{qm} for this system is rather small compared to that for PTSA quenched with negative ions (I^- or SCN^-). This is in contrast to the quenching rate constant in homogeneous medium where quenching of PTSA with Cu^{2+} is the most effective (Table XXIV). For water concentrations above R = 11 (the maximal hydration of the polar headgroups) the fluorescence decay for PTSA/Cu^{2+} becomes one-exponential : k_{qm} is too small and equation (1) reduces to equation (13).

Hence, for the determination of aggregation numbers, the system PTSA/Cu^{2+} is only useful for small aggregates. Under the experimental condition B only values for k_e were obtained. The values for k_e given in table XX are not the real ones, since the approximation $k_e[M] \ll k_{qm}$ was used in their calculations. Because of the low k_{qm} for this probe/quencher system, this approximation certainly does not hold for those large aggregates.

Table III : Quenching rate constants for the four probe/quencher systems in homogeneous aqueous medium.

System	k_q ($\times 10^{-9} M^{-1} s^{-1}$)
PTSA/Cu^{2+}	5.7
PTSA/I^-	4.0
PTSA/SCN^-	3.1
PSA/Cu^{2+}	3.5

In addition to this electric field, viscosity also restrains the mobility of ions in a micellar interior. The microviscosity decreases radially from the interphase to the centre of the micel. Near the interphase there is a high concentration of hydrated ions while the characteristics of the water in the centre of the aggregates ressemble that of "free" bulk water.

For this reason, the quenching rate constant of systems located at the interphase - see PSA/Cu^{2+} - is smaller compared to those located in the centre of the waterpool - see PTSA/I^- and PTSA/SCN^-. There is no analogous difference for their quenching rate constant in homogeneous medium (Table III).

The difference of k_{qm} for PTSA/I^- and PTSA/SCN^- reflects the difference of their quenching rate constants in homogeneous aqueous medium (k_q).

Not only a high k_{qm} value is necessary when searching an effective probe/quencher combination in the fluorescence quenching method, but also its relation to $k_e[M]$, the exchange process, is important.

The results further indicate that the rate of intermicellar exchange increases with the concentration of solubilized water. For small aggregates, $k_e[M]$ is rather low while k_{qm} for each probe/quencher system here considered is high so that $k_e[M] \ll k_{qm}$. For larger aggregates, k_{qm} decreases while the exchange rate increases. At a certain aggregate size, depending on the nature of the surfactant (k_e) and the probe/quencher system (k_{qm}), $k_e[M] \approx k_{qm}$. The intermicellar exchange and the quenching are two competing processes. An exchange can be followed by a quenching or by another exchange. In this case, no correct values for N_{agg}, k_e and k_{qm} can be obtained from the non-exponential decays.

Since k_{qm} for PTSA/I^- is one order of magnitude larger than for PSA/Cu^{2+}, PTSA/I^- can characterize aggregates of AOT with R = 20, while PSA/Cu^{2+} fails already at R = 12. The system PTSA/KSCN is slightly less effective than PTSA/I^-, due to its slightly lower k_{qm}.

Further increasing the size of the aggregates leads to a situation where k_e [M] $> k_{qm}$. The fluorescence decay is one-exponential (experimental condition B). The kinetic scheme proposed that explains a non-exponential decay of a probe in a micellar solution is based on a Poisson distribution of probes and quenchers over the aggregates. Because of a very fast exchange of probes and quenchers, this distribution according to a Poisson distribution function is destroyed during the lifetime of the probe. Each probe senses an average concentration of quenchers. For these aggregates only a value for k_e and the product $k_{qm}.N_{agg}$ can be obtained.

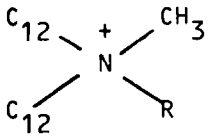
The size of the aggregates for which the fluorescence decay becomes one-exponential is a function of the probe/quencher system. For PSA/Cu^{2+} this is at R = 20 while for PTSA/I^- the decay is one-exponential for R = 30. Not only the smaller k_{qm} but also the lifetime of the probe is responsible for the difference between these two systems.

The fluorescence lifetime of the probe determines the window within which dynamic processes can be observed. The longer the lifetime, the more exchanges between micelles are observed. These exchanges counteract the Poisson distribution, and this effect is larger for the long living probe PSA than for the short living PTSA.

Because of its long fluorescence lifetime, slower dynamic processes can be measured with PSA compared to PTSA. While PTSA can only determine exchange processes with $k_e > 5.10^9 M^{-1}s^{-1}$, PSA can measure exchange rate constants for the smaller aggregates too (R < 11).

IV. AGGREGATION NUMBER AND RATE OF EXCHANGE

Fluorescence quenching study with PSA/I^- in the cationic inverted micellar systems of



1. Structural variations

with R = $-CH_2-CH_2-OH$: DDEAc

$-CH_2-CH_2-O-C(=O)-C(CH_3)=CH_2$: DDAcr.Ac

$-CH_2COOH$: DDzAc

$-CH_3Cl^-$: DDAC

$-CH_3Br^-$: DDAB

All these surfactants were studied at 0.08 M in toluene.

Table IV lists the values of N_{agg} for the five surfactants at R-values that are indicated.

Table IV : N_{agg} values for the different cationic inversed micellar systems at given R values.

R/Detergent	DDEAc	DDAC	DDAB	DDzAc	DDAcr.Ac.
1	17	8	7	19	
2,5	20	12			33
4	30	19			

The interaction of H_2O molecules with the polar headgroup seems to have a substantial influence on the size of the aggregates. H_2O molecules have a much larger opportunity to interact with the headgroup of DDEAC than with the headgroups of DDAC and DDAB. More monomer units are kept together via the water molecules that form intermolecular hydrogen bridges, so that N_{agg} increases. For each surfactant system the N_{agg} also increases if the amount of water increases. There is only a small difference between DDAC and DDAB. The larger Br^- ion seems to shield the ammonium headgroup from more water molecules more effectively than does the smaller Cl^- ion.

The effect of the structural variation in four different surfactant systems on the values of k_e is given in table V.

Table V : Influence of structural variation of four different surfactant systems on the values of k_e.

Surfactant	R	k_e ($10^8 M^{-1} s^{-1}$)
DDAC	1	1,2
DDEAc	1	1,5
DDAB	1	1,9
DDAcr.Ac	2,5	2,3

From R = 1 till R = 4 k_e is a constant value. At a water content smaller than the maximum hydratation, the exchange rate remains constant. The value for the rate constant of exchange in the DDEAC system was too small to be measured at room temperature and a study of temperature dependence had to be made (vide infra).

From this table it is evident that enhancing the interaction of water molecules with the headgroups leads to the formation of more stable inverted micelles.

2. Effect of additives on size and stability

Table VI reports the aggregation numbers and rate constants of exchange for 0.08 M DDEAC aggregates in toluene using glycerol and formamide as polar additives.

Table VI : Influence of additives on the aggregation behaviour of DDEAC

R	N_{agg}	k_e
0.9 glycerol	13	$2.9\ 10^8$
0.8 formamide	10	$1.9\ 10^8$
1.0 H_2O	17	$0.7\ 10^8$

For both systems the aggregation numbers are smaller than in the case of water as additive, and the rate constants of exchange are larger. The inverted micelles formed are thus smaller and less stable.

3. Temperature dependent quenching study

Three of the systems discussed above (DDEAC, DDAC, DDAB) were investigated as a function of temperature.

The results indicate that increasing the interaction of water with the polar headgroup of the surfactant (DDEAC as DDAC) results in a decrease of the activation entropy change for exchange.

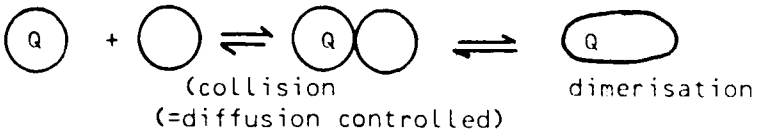
$$\Delta S^{\neq} = \begin{cases} 200\ J\ M^{-1}K^{-1} & (DDEAC) \\ 250 & (DDAC) \end{cases}$$

For DDEAC the value of $\Delta S^{\neq}$ is smaller than for DDAC. Because there is a favorable interaction between the water molecules and the head group of DDEAC, the surfactant molecules have less tendency to migrate into the organic solvent and form soluble monomer units. As the degree of organization diminishes more efficiently in DDAC the entropy factor is larger than for DDEAC. However, it should be stressed that this is not the only factor that influences the entropy. Also the structure of the interphase plays an important role. This has been stated in the literature for the AOT system. The surfactant molecules having 2 tails form inverted micelles with a more viscous layer so that the diffusion of the monomer units is also less efficient. This too has a large effect on the entropy factors.

We also evaluated the results of a temperature dependent study of the DDEAC/Toluene system using glycerol and formamide as polar additives. For both systems the N_{agg} is not dependent upon temperature. Both k_e and k_{qm} are influenced by changing the temperature. The value for the activation enthalpy of exchange is considerably smaller than the respective value for H_2O.
The cationic surfactant molecules and counterions are separated less efficiently in these organic additives than in the case of H_2O. Enhancing the temperature will also have an additional effect on the dissociation of the contact ion pairs. If the dissociation becomes more important, then the repulsion between the positively charged headgroups will be more important too. This effect results in less stable inverted micellar aggregates.

V. STABILIZATION OF INVERTED MICELLAR SYSTEMS : THE MEANING OF k_e

The intermicellar exchange of quenchers and/or probes can be visualised by following scheme :



(collision (=diffusion controlled)

dimerisation

separation

At very low water concentration (<hydratation of the surfactant molecules), the value of k_e equals about 10^8 $M^{-1}s^{-1}$. Adding water results in a decrease in the resistance of the micellar units against dimerisation.

A temperature study allows calculation of $\Delta H_e^{\neq}$ and $\Delta S_e^{\neq}$ values according the relationship of Van 't Hoff. These values are given in table VII for the different investigated detergents.

Table VII : Values for the activation enthalpy and entropy for the exchange process (k_e) in inversed micellar systems.

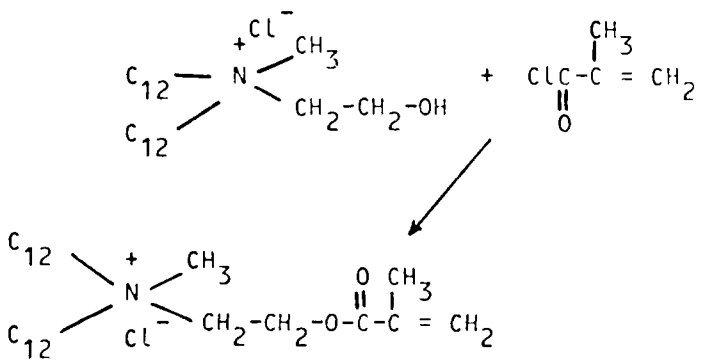
Surfactant	R	$\Delta H_e^{\neq}$ (kJmol)	$\Delta S_e^{\neq}$ ($JK^{-1}mol^{-1}$)
DDAC	1	35	280
DDAC	8,5	17	220
AOT	10	70	93
DDAcr.Ac	2,5	22	230
DDAB	1	30	260
DDEAc	1	19	220

Obviously from these results one learns that the AOT aggregates are more resistive against dimerisation than these of DDAC. This higher activation enthalpy is ascribed to the stiff geometry of AOT what provides a sterical hindrance for the pushing together of the monomers in a micel.

A smaller $\Delta H_e^{\neq}$ value indicates a better shielding of the charge of the ammonium groups like e.g. DDEAc versus DDAC. The exchange of a CH_3 by a $-CH_2-CH_2-OH$ group, that interacts probably more strongly with H_2O molecules, is responsible for this shielding effect. These results are also giving evidence for a correlation between the amount of electrical repulsion between the headgroups and the value of $\Delta H_e^{\neq}$; this is also supported by the difference in $\Delta H_e^{\neq}$ value between DDAC and DDAB : Br^- screens better a positive charger than Cl^-.

The exchange rate constants for all the surfactant systems studied are all of the same order of magnitude : between $10^8 M^{-1} s^{-1}$ and $3 \times 10^8 M^{-1} s^{-1}$.

One of the detergent molecules, DDAcr.Ac, has been synthesized from DDEAc, using methacryloylchloride :



In this way a polymerizable part is introduced. Further work in this domain is going on in the research group of our laboratory.

Application of the fluorescence quenching method allows the determination of the rate of exchange of probe and/or quencher (k_e) what is a measure for the stability of the reversed micellar system.

END

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DTIC